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## (54) DETERGENT COMPOSITIONS

(71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London E.C.4, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This detergent relates to detergent compositions which are of particular value in the washing of polyester-containing fabrics.

It is known that some fabrics made of synthetic materials present special problems in the removal of oil-based soils from their surface. Polyester materials, for example polyethylene terephthalates, demonstrate this problem, alleviation of this problem will be referred to hereinafter as "soil-release".

Copolymers of polyoxyethylene glycol and polyethylene terephthalate, used in the range from 2:1 to 10:1, have previously been proposed, in UK patent specification 1,088,984, as polyester textile finishing agents. The use of these copolymers, as antiredeposition agents, in fabric washing procedures is disclosed in UK patents specification 1,154,730 and it is stated that the copolymers may be used in conjunction with any of the known types of anionic, nonionic and cationic detergents normally used in laundering operations. Among the nonionic detergents are polyethenoxy derivatives of alcohols and the present invention proposes the use of the copolymers either individually or as mixtures thereof in admixture with specific nonionic materials to give washing liquors having particularly favourable soil release properties. When polyester-containing fabrics are washed in liquors containing the mixtures of the invention the fabrics are modified so that oil containing stains subsequently formed on the fabric are more easily removed on subsequent washing. The invention provides detergent powders and liquids which will be used to form a wash liquor, as well as a wash liquor prepared *in situ* by the separate addition of the two compounds required to be present together. A detergent powder or liquid will pre-

ferably contains up to 2% by weight of the polymer. The invention also extends to laundering processes using these mixtures of polymer and nonionic active.

The specific nonionic detergents aforementioned are:

- (a) ethoxylated alkyl phenols wherein the total alkyl substituents contain from 6 to 12 carbon atoms, and the ethylene oxide (EO) is present in the molar ratio from 5:1 to 25:1 with reference to the alkyl phenol.
- and
- (b) condensation products of from 5 to 30 (preferably 5 to 20) molar ratios of ethylene oxide with 1 molar ratio of an aliphatic alcohol selected from
  - i) straight chain saturated aliphatic alcohols with from 10 to 16 carbon atoms,
  - ii) branched chain saturated aliphatic alcohols with from 10 to 20 carbon atoms,
  - iii) branched unsaturated aliphatic alcohols with from 10 to 20 carbon atoms, and
  - iv) straight chain unsaturated aliphatic alcohols with from 10 to 18 carbon atoms.

The preferred nonionic detergents are:

- octyl phenol condensed with from 5 to 12 EO units,
- nonyl phenol condensed with from 5 to 15 EO units,
- C<sub>13</sub> secondary aliphatic alcohols condensed with from 3 to 12 EO units, and
- C<sub>13</sub> secondary aliphatic alcohols condensed with from 5 to 12 EO units.

Detergent formulations of the invention may contain detergents other than the nonionic detergents defined previously. The Applicants have found that relatively small amounts of soap (alkali-metal salts of long chain fatty acids) or other anionic detergents decrease the soil release effect obtained by the practice of the present invention. Other types of detergents outside the above definition, for example

nonionic, amphoteric or zwitterionic, can be present in relatively large proportion without serious loss of the soil release properties. Thus use of a mixture of nonionic detergents, the mixture containing detergents both within and outside the above definition, will provide the soil release properties of the invention. The Applicants have found, for example, that the addition of up to 80%, preferably not more than 40% (by weight of the nonionic) of dodecyl benzene sulphonate can be tolerated while still obtaining a useful technical effect. Larger proportions of nonionic detergents outside the definition can be tolerated.

The detergent compositions of the invention will contain the other required or optional components for example builder materials, examples of which are sodium tripolyphosphate, sodium orthophosphate, sodium carbonate, salts and esters of sulphonated fatty acids, salts of nitrilotriacetic acid, salts of ethylene diamine tetraacetic acid and phosphonate derivatives thereof, oxidised starches and polymeric builders for example polycarboxylates; other detergent active materials, silicate materials (which may be included as builder materials), other antiredeposition agents for example sodium carboxymethylcellulose and polyvinylpyrrolidone, fluorescers, germicides, enzymes, bleaches. The solid form of the composition will not be limited and any of the forms known in the field are available for example pellets, powders, flakes and extruded forms. The invention is also applicable to liquid compositions.

In a preferred solid formulation the copolymer is mixed with an organic extrudable solid to form granules. The technique used is that described in UK specification 1204123.

Examples of the composition of the invention will now be given. The following test method was used to evaluate the soil release effect.

#### Test Method

Approximately 25g bulked polyester fabric was treated by washing five times in 450 ml of a wash liquor containing 0.05% of a detergent from the defined range of surfactants and 0.10% sodium tripolyphosphate. The washes were carried out in the Launder-O-Meter (Atlas Electric Devices Co., Chicago) both in the absence and presence of a suitable level of

polymer for 10 minutes at 50° C and a water hardness of 24° H with rinsing and drying between washes.

Samples (~ 1.5g) of the treated fabric were stained in a standard manner from a microscope slide onto which approximately 0.035g dirty sump oil had been evenly spread. After ageing for approximately 15 minutes, two stained pieces were washed together once in the Terg-O-Tometer (United States Testing Co. Inc. Hoboken NJ) in 1 litre of the same surfactant system as in the pre-treatment. Following rinsing and drying, the samples were graded visually against standard strains with a rating from 0 to 7 where 0 represents the stained unwashed fabric and 7 the clean new fabric.

#### Example I.

A sump oil soil release test was performed using the method described and using a polymer prepared from polyethylene terephthalate and polyoxyethylene glycol (mol wt 1540) in the ratio 2:1. The detergent used was a C<sub>15</sub> secondary aliphatic alcohol 9EO. The test score recorded was 5 indicating a good soil release effect. On fabric washed in the absence of the polymeric additive the test score was 1.

#### Example II.

Example I was repeated using a polymer with a ratio polyethylene terephthalate to polyoxyethylene glycol of 7:2. A score of 7 was recorded indicating an excellent soil release effect.

#### Example III.

Example I was repeated using a polymer with a ratio polyethylene terephthalate to polyoxyethylene glycol of 5:1. A score of 5 was obtained.

#### Example IV.

Example II was repeated using nonyl phenol 5EO as the detergent. A score of 7 was recorded indicating an excellent soil release effect. On fabric washed in the absence of polymeric additive the test score was 1.

#### Example V.

Example II was repeated using a C<sub>14</sub> primary aliphatic alcohol 3EO as the detergent and a level of polymer of 0.003%. The test score recorded was 3. On fabric washed in the absence of the polymeric additive the test score was 0.5.

Other Examples are quoted in Table I.

TABLE I

Polymer	Polymer Level %	Detergent	Soil- Release Rating with Polymer	Control
<u>VI</u>				
Polyethylene terephthalate, polyoxyethylene glycol (mol wt 600) in the ratio 3:1	0.0015	C <sub>15</sub> secondary aliphatic alcohol 9EO	6	1
<u>VII</u>				
Polyethylene terephthalate, polyoxyethylene glycol (mol wt 400) in the ratio 7:2	0.0015	C <sub>15</sub> secondary aliphatic alcohol 9EO	3	1
<u>VIII</u>				
As in Example II	0.0030	C <sub>15</sub> secondary aliphatic alcohol 7EO	7	1
<u>IX</u>				
As in Example II	0.0030	C <sub>15</sub> secondary aliphatic alcohol 12EO	5	1
<u>X</u>				
As in Example II	0.0030	C <sub>15</sub> secondary aliphatic alcohol 15EO	4	2
<u>XI</u>				
As in Example II	0.0030	C <sub>13</sub> secondary aliphatic alcohol 3EO	4	1
<u>XII</u>				
As in Example II	0.0030	C <sub>13</sub> secondary aliphatic alcohol 9EO	6	1
<u>XIII</u>				
As in Example II	0.0030	C <sub>14</sub> primary aliphatic alcohol 9EO	3	0

TABLE I (continued)

Polymer	Polymer Level %	Detergent	Soil- Release Rating with Polymer	Control
<u>XIV</u>				
As in Example II	0.0015	Nonyl phenol 10EO	6	1
<u>XV</u>				
As in Example II	0.0015	Nonyl phenol 12EO	6	1
<u>XVI</u>				
As in Example II	0.0015	Nonyl phenol 14EO	6	1

Examples which illustrate the deleterious effect of anionic surfactants on soil release properties are given in Table II.

TABLE II

Polymer	Polymer Level	Surfactant Level	Detergent	Soil-Release Rating with Polymer	Control
<u>XVII</u>					
As in Example II	0.0015	0.05	C <sub>15</sub> secondary aliphatic alcohol 9EO	7	1
<u>XVIII</u>					
As in Example II	0.0015	0.045 0.005	C <sub>15</sub> secondary aliphatic alcohol 9EO Dodecyl benzene sulphonate	6	1
<u>XIX</u>					
As in Example II	0.0015	0.035 0.015	C <sub>15</sub> secondary aliphatic alcohol 9EO Dodecyl benzene sulphonate	4	1
<u>XX</u>					
As in Example II	0.0015	0.025 0.025	C <sub>15</sub> secondary aliphatic alcohol 9EO Dodecyl benzene sulphonate	2	1
<u>XXI</u>					
As in Example II	0.0015	0.05	Dodecyl benzene sulphonate	1	1

The following nonionic detergents are not included in the defined class.

	Dirty Sump Oil Rating	
	With Polymer	Without
N,N dimethyl cocoamine oxide	2.5	1
N,N dimethyl hardened tallow amine oxide	2	1
N,N (2-hydroxymethyl) cocoamine oxide	2.5	1
Hardened tallow alcohol 10EO	0	0
Hardened tallow alcohol 25EO	0	0
Hardened tallow ethanolamide 4EO	2.0	2.0
Hardened tallow ethanolamide 14EO	2.0	2.0

## WHAT WE CLAIM IS:—

1. A detergent formulation containing a copolymer of polyoxyethylene glycol and polyethylene terephthalate and a nonionic detergent selected from the groups
  - (a) ethoxylated alkyl phenols wherein the total alkyl substituents contain from 6 to 12 carbon atoms, and the ethylene oxide (EO) is present in the molar ratio from 5:1 to 25:1 with reference to the alkyl phenol, and
  - (b) condensation products of from 5 to 30 molar ratios of ethyleneoxide with 1 molar ratio of an aliphatic alcohol selected from
    - i) straight chain saturated aliphatic alcohols with from 10 to 16 carbon atoms,
    - ii) branched chain saturated aliphatic alcohols with from 10 to 20 carbon atoms,
    - iii) branched unsaturated aliphatic alcohols with from 10 to 20 carbon atoms, and
    - iv) straight chain unsaturated aliphatic alcohols with from 10 to 18 carbon atoms.
2. A detergent formulation as claimed in claim 1 wherein the nonionic condensation product (b) contains from 5 to 20 molar ratios of ethylene oxide per molar ratio of the aliphatic alcohol.
3. A detergent formulation as claimed in claim 1 or 2 wherein the aliphatic alcohol contains from 12 to 15 carbon atoms.
4. A formulation as claimed in claim 1, 2 or 3 wherein the nonionic detergent is
  - octyl phenol condensed with from 5 to 12 EO units,
  - nonyl phenol condensed with from 5 to 15 EO units,
  - C<sub>13</sub> secondary aliphatic alcohols condensed with from 3 to 12 EO units,
  - C<sub>15</sub> secondary aliphatic alcohols condensed with from 5 to 15 EO units.
5. A method of washing textiles wherein the textiles are contacted with a wash liquor containing a copolymer of polyoxyethylene glycol and polyethylene terephthalate and a nonionic detergent selected from the groups defined in claim 1.
6. A method of washing textiles as claimed in claim 5 wherein the nonionic detergent is as defined in claim 2.
7. A method of washing textiles as claimed in claim 5 wherein the nonionic detergent is as defined in claim 3.
8. A method of washing textiles as claimed in claim 5 wherein the nonionic detergent is as defined in claim 4.
9. A detergent formulation as claimed in claim 1, 2, 3 or 4 wherein the copolymer is admixed with an organic extrudable solid to form granules.
10. A detergent formulation as claimed in claim 1 with reference to any of the Examples.

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